

Some Double Chlorides
of Ferric and of Ferrous Iron with Some
Aromatic Bases

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

RAPHAEL MONROE MCKENZIE

1896

EASTON, PA.
CHEMICAL PUBLISHING CO.
1896

Some Double Chlorides
of Ferric and of Ferrous Iron with Some
Aromatic Bases

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

RAPHAEL MONROE McKENZIE

1896

EASTON, PA.
CHEMICAL PUBLISHING CO.
1896



Digitized by the Internet Archive
in 2026

CONTENTS.

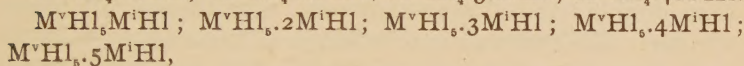
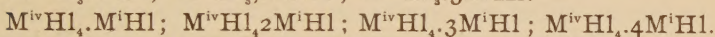
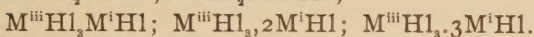
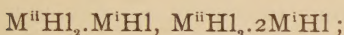
Introduction	5
Double Halides of Iron Previously Described	7
Preparation of Materials	8
Testing of Methods of Analysis ; Iron, Chlorine and Water	9
Atomic Weights Used in this Work	12
Oxidation of the Organic Bases by Ferric Chloride	13
Summary of the Compounds Obtained	16
Preparation of the Salts for Analysis and the Results of the Analyses	16
Description and Formation of the Compounds	17
<i>Dianiline Chlorferrate</i>	17
<i>Hydrous Dianiline Chlorferrate</i>	18
<i>Hexaniline Chlorferrate</i>	19
<i>Hydrous Hexaniline Chlorferrate</i>	24
<i>Hexaorthotoluidine Chlorferrate</i>	24
<i>New Method of Preparation</i>	26
<i>Dimetatoluidine Chlorferrate</i>	29
<i>Trimetatoluidine Chlorferrate</i>	32
<i>Triparatoluidine Chlorferrate</i>	34
Salts from Ferrous Chloride	36
<i>Salts from Ferrous Chloride and Aniline Hydrochloride</i>	36
<i>Dianiline Chlorferrite</i>	38
<i>Triorthotoluidine Chlorferrite</i>	40
<i>Hexaorthotoluidine Chlorferrite</i>	41
Preparation of the Salt in an Atmosphere of Hydrogen	44
Further Work on Aniline Hydrochloride and Ferrous Chloride	50
Conclusion	52
Biographical	53

ACKNOWLEDGMENT.

This investigation was undertaken at the suggestion of Professor Remsen, and was carried out under his direction. I wish to acknowledge here my indebtedness to him for suggestions in the course of the work and for encouragement in time of trouble. I wish also to thank Professor Morse and Dr. Ames for instruction and help in the preparation for the doctorate.

INTRODUCTION.

The subject of double halides was discussed in an article¹ by Professor Remsen in 1888, in which the history of the double halides was reviewed together with the views previously held in regard to them. He showed that almost all the double salts mentioned in the literature—in all over four hundred—could be arranged in a few simple groups which might be represented by the following types :



in which M^x represents any polyvalent metal, and M^i any alkali metal.

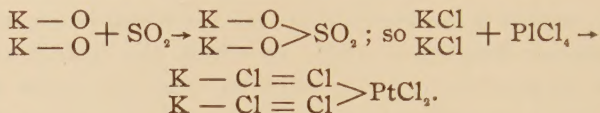
From this study the generalization was drawn that “when a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of alkali salt which are added to one molecule of the other halide, is never greater and is generally less than the number of halogen atoms combined in the latter.” If the halogen atoms are considered as trivalent, then “two halogen atoms together can play the same part that the so-called linking oxygen atom plays in the oxygen salts;” thus the double halides were rescued from the vague ranks of molecular compounds, and given a place among the atomic compounds.

Double halides like potassium chloroplatinate, K_2PtCl_6 , which under the old view were considered as molecular compounds of two molecules of potassium chloride and one molecule of platinic chloride, $2KCl.PtCl_4$, are now considered as salts of definite chloro acids, as the hydrochloroplatinic acid, H_2PtCl_6 .

Just as acidic oxides unite with basic oxides to form salts, so acidic halides unite with basic halides to form double hal-

¹ Am. Chem. Jour., II, 291.

ides. This similarity between the oxygen salts and the double halides is seen from the following formula :



A thorough investigation of those compounds given in the literature, which did not fall under this rule, was undertaken by students working under Professor Remsen. The work was also carried further in order to obtain all the double halides of the metals under investigation that could possibly be formed under any conditions. In the course of this study some double halides¹ were discovered that did not fall under the law. Therefore an extension of the law was made to include these and some salts, as $\text{CuCl}_2.2\text{KCl}$ and $\text{CdCl}_2.4\text{KCl}$, which had long been known. Some other double halides of cadmium and of zinc have since been brought out by Wells and Walden,² and by Wells and Campbell,³ which do not fall under the law as first expressed.

According to the extension of the law, three halogen atoms can act together to form a trivalent group, thus— $\text{Cl} < \begin{array}{c} \text{Cl} - \\ | \\ \text{Cl} - \end{array}$.

Then the salts like potassium chlorocuprite, $\text{CuCl}_2.2\text{KCl}$, are represented thus, $\text{Cu} - \text{Cl} < \begin{array}{c} \text{Cl} - \text{K} \\ | \\ \text{Cl} - \text{K} \end{array}$.

It appears from the work of Saunders⁴ that double halides do not form from halides of two metals belonging to the same natural group.

The work on the double halides has been extended into the field of organic chemistry by the use of the substituted ammonias of the aromatic series in place of ammonia. Such double halides of tin, mercury, antimony, zinc and cadmium have been studied in this laboratory. It is to this part of the

¹ Am. Chem. Jour., 14, 85-87.

² Am. Jour. Sci., Dec., 1893.

³ *Ibid.*

⁴ Am. Chem. Jour., 14, 151.

general work on double halides that this investigation pertains.

DOUBLE HALIDES OF IRON PREVIOUSLY DESCRIBED.

A search of the literature up to the fall of 1894 was made, to find what double halides of iron with halides of inorganic and of organic bases had been prepared. No double halides of iron with halides of organic bases had been prepared, and those with the halides of the metals had not been thoroughly investigated.

The salts given in the Jahresbericht up to 1889, and in the other journals up to 1894 are :

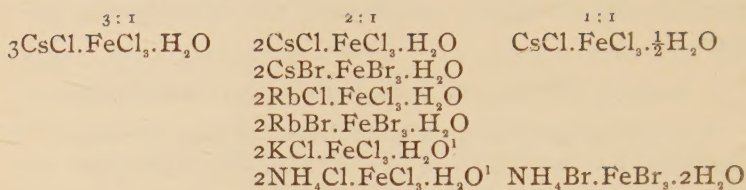
$2\text{KCl} \cdot \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	} Fritzsche, Jour. Prakt. Chem., (Erdmann) 18, 483.
$2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	
$2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	Genth, G., Jahresberichte, 1857, 224.
$2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	Hensgen, " 1878, 1781.
A caesium salt, (No analyses given).	{ Lehmann, Zeit. f. Krystallogr, 10, 336.
$2\text{KCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	} Neumann, G., Ann. 244, 333.
$2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	
$2\text{RbCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	
$\text{MgCl}_2 \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	
$\text{BeCl}_2 \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	
$3\text{RbCl} \cdot \text{FeCl}_3$	} Godeffroy, Arch. Pharm. [3], 9, 345.
$2\text{NaCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$	

In the fall of 1894 there was published the results of a systematic study by Walden,¹ of the double halides of ferric iron with rubidium, caesium, potassium and ammonium, in relation to the theory regarding the double halides.

He did not mention the work of Neumann, which was the best work previously published, and he gives the salt $2\text{RbCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$, obtained by Neumann, as a new compound. The salt $3\text{RbCl} \cdot \text{FeCl}_3$, described by Godeffroy, was not obtained in this work; and Walden thinks that Godeffroy must have had the salt $2\text{RbCl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$.

The salts obtained by Walden are :

¹ Am. Jour. Sci., [3], 48, 283.



PREPARATION OF MATERIALS.

The ferric chloride was prepared by dissolving piano wire in an excess of pure hydrochloric acid and oxidizing the solution of the ferrous chloride formed by passing into it a stream of chlorine gas until no reaction for ferrous iron could be detected with potassium ferricyanide. This solution was then repeatedly evaporated to crystallization to drive off all chlorine. Just enough dilute hydrochloric acid was added to prevent the separation of ferric chloride at ordinary temperatures; and the amount of ferric chloride in 1 cc. of the solution was determined. Another solution of ferric chloride was prepared by diluting 100 cc. of the concentrated solution up to 250 cc.

In the earlier part of the work, saturated solutions of ferrous chloride were prepared from piano wire, and the content, in ferrous chloride at a definite temperature, was determined; but they could not be kept free from ferric chloride. The same trouble attended the use of the crystallized ferrous chloride.

In the latter work the ferrous chloride was obtained by dissolving the calculated amount of iron wire in an excess of hydrochloric acid, in the vessel in which the double salt was to be made.

Aniline hydrochloride was prepared by treating 5 parts by volume of redistilled aniline with 6 parts by volume of pure concentrated hydrochloric acid. The aniline hydrochloride, which separated on cooling, was filtered off by aid of the pump and dried on a porous plate or by pressing between filter paper in a press.

The toluidine hydrochlorides were prepared in the same manner as the aniline hydrochloride.

¹ Previously described by Fritzsche.

METHODS OF ANALYSIS.

Iron.—Since the conditions were complicated by the presence of organic matter, the ordinary methods for the analysis of iron could not be used. Much time and work were therefore required to obtain a satisfactory method of analysis for these salts. A method was sought which would permit the determination of both the iron and the chlorine in the same sample, but without success. For the testing of methods weighed amounts of the ferrous ammonium sulphate and of aniline hydrochloride were mixed and analyzed. Such mixtures were fused with sodium potassium carbonate and a little potassium nitrate to oxidize organic matter. The oxide, after being filtered off and washed, was weighed as ferric oxide; but the method gave results that were too high by 0.5–1.5 per cent. This was due, no doubt, to the presence of alkaline salt retained by the ferric oxide.

Other weighed mixtures were fused with potassium pyrosulphate; the ferric sulphate formed was reduced with zinc and sulphuric acid and was titrated with a solution of potassium permanganate. This method was discarded because the pyrosulphate was not a sufficiently strong oxidizing agent; unburned carbon was left in the melted mass and the fused mass frothed over the edge of the crucible. Further objections were the length of time consumed in the reduction with zinc, and the fact that the presence of any organic matter invalidated the results.

To obtain satisfactory results by precipitation of the iron from the double salts with potassium hydroxide, a second precipitation with ammonia was required to free the ferric oxide from the alkali. This method, though exact, was too long where so many analyses were to be made.

Attempts were also made to destroy the organic matter by oxidation with fuming nitric acid, and with potassium chlorate and hydrochloric acid; but substituted benzene compounds were formed which resisted complete oxidation.

The method finally adopted was the following: The weighed salt was dropped into a porcelain dish containing a

excess of a weak solution of pure potassium hydroxide. The dish was then heated on a sand-bath until the solution no longer gave any odor of aniline or of toluidine—water was added from time to time as required. The solution was then neutralized with hydrochloric acid and an excess of the acid was added. As in many cases the ferric hydroxide had been partially reduced by action on the aniline, a small amount of hydrogen peroxide was added, and the solution was then evaporated just to dryness. A little more acid was now added, and it was again evaporated to dryness. In the case of ferrous salts the oxidation with hydrogen peroxide was always required. The ferric chloride was then filtered into a pressure-bottle through washed asbestos, to separate any precipitate formed by action on the aniline. The filtrate was then treated with a solution of potassium hydroxide until a slight permanent precipitate of ferric hydroxide separated; 0.2 cc. of dilute hydrochloric acid was added, and 1 gram of potassium iodide was introduced. The bottle was then closed and heated at about 60° for twenty minutes. After cooling, the iodine set free was titrated in the bottle by use of starch and a solution of sodium thiosulphate, 1 cc. of which corresponds to 1 milligram of iron. The results were quite satisfactory.

The use of an open dish in place of a flask when boiling off the aniline or toluidine greatly lessened the time required. The use of the open dish and the evaporation of the ferric chloride to dryness were found necessary to ensure the complete removal of the hydrogen peroxide. The hydrogen peroxide is more stable than was formerly supposed.¹ It was found that hydrogen peroxide passed off with the steam and condensed on the side of a flask running back into the solution and causing error in analysis. The water which condensed on a watch-glass held in the steam above the flask also gave a strong reaction for hydrogen peroxide when tested with iodized starch paper.

Chlorine.—In the first part of the investigation the chlorine was determined gravimetrically; but as dilute solutions of

¹ Ber. d. chem. Ges., 27, 3307.

the ferric double halides react to form precipitates and colored solutions, the precipitation of the chlorine was not entirely satisfactory.

The Volhard method was tried with a solution of a ferric double halide acidified with nitric acid; but it could not be used thus, as the end reaction with the thiocyanate was masked by the colored products formed. Then the lime method was tried, but the presence of the nitrogen necessitated the use of soda-lime. As the soda-lime contained a large amount of the halides, a mixture of sodium carbonate and lime, as suggested by S. W. Johnson,¹ was tried. But just then a more satisfactory method was obtained and these trials were discontinued.

The method finally employed was the following: A weighed sample of the salt was dropped into an Erlenmeyer flask containing a solution of pure potassium hydroxide, which was in excess of the amount required to decompose the salt. The alkaline solution was then boiled until the odor of aniline or toluidine was no longer noticed in the steam given off. Then the solution, formed on dissolving the ferric hydroxide in an excess of nitric acid, remained colorless. If all the organic base had not been driven off with the water vapor, a colored solution was formed. To the acid solution 5 cc. of a saturated solution of ferric ammonium alum was added, and the cold solution was titrated by Volhard's method in the flask.

In the case of the ferrous salts, a cold solution of the salt in very dilute nitric acid could be titrated directly without boiling off the organic base. But in most cases the method given above was used.

Water of Crystallization.—All attempts to make quantitative determinations of the water in these salts were unsuccessful. Samples of the salts, placed in the sulphuric acid desiccator, did not come to constant weights even after standing more than a month. It was found that the inside of the desiccator and the watch glass containing the salt became coated with a sublimate.

¹ Ann. Chem., 169, 69.

Samples of the salts were heated from 90–110° C. in a glass tube, the closed end of which was placed in an air-bath while the other end extended out into the air. Here it was found that a sublimate was deposited on the cool part of the tube. These trials showed that the water could not be determined by difference.

It was then thought that the water might be determined by absorption in a drying tube. To try this a sample of the salt was heated in a porcelain boat, within a glass tube, which extended through an air-bath. Air was drawn slowly through the tube while the air-bath was heated to 100° C.; when it was found that the aniline hydrochloride and also the toluidine hydrochloride sublimed and was deposited on the cooler parts of the tube, while the water was carried farther to still colder portions of the tube. To test whether water alone was carried on by the air current, a U-tube, containing a solution of silver nitrate, was attached to the front end of the tube and the air was drawn through it. After a few minutes the solution became cloudy and a precipitate formed, showing that compounds containing chlorine were carried over. This prevented further attempts being made to determine the water quantitatively.

The presence or absence of water was determined qualitatively, thus: The combustion tube was united to a drying tube, at the back, and to an empty dry U-tube, and this to a drying tube, at the front. The U-tube was cooled by placing it in cold water. The salt was heated in the porcelain boat as before, and air was drawn through the system. If the salts contained water it was deposited on the walls of the U-tube as dew or in drops; the amount deposited giving some idea of the proportion of water in the salt and confirming the analytical results.

Some of the salts were analyzed before this method was used and in these cases nothing has been said as to the water, though the analytical results require the assumption that water was contained in them.

The atomic weights used in the calculation of the formulas

for the salts were the following: H, 1; O, 16; N, 14; Cl, 35.4; Fe, 56; C, 12.

It was found that the differences in the more complex formulæ, when calculated with these and when calculated with the more exact atomic weights were not more than a tenth of one per cent.

OXIDATION BY FERRIC CHLORIDE.

Much difficulty was experienced in the early part of the work, owing to the tendency of ferric chloride to oxidize the organic base. Thus, when a solution of ferric chloride and aniline hydrochloride was heated, the action which took place was the decomposition¹ of the aniline hydrochloride and the reduction of the ferric chloride to ferrous chloride. In many cases a blue flocculent precipitate separated in such quantity as to fill the solution. In other cases it separated in smaller amounts, but interfered with obtaining pure salts. Slightly acid solutions were made in the ratio of one molecule of ferric chloride to two molecules of aniline hydrochloride, of one molecule of ferric chloride to four molecules of aniline hydrochloride, and of one molecule of ferric chloride to five molecules of aniline hydrochloride. The first solution was colored a light green on mixing and darkened on heating, when it became filled with the blue precipitate. The second solution with a smaller proportion of ferric chloride was a lighter green than the first, but on heating and standing it darkened and the precipitate formed. The third solution was a yellowish green color on mixing, but on heating, the upper layer exposed to the air, became green; then the precipitate started to form and soon spread through the whole solution.

It was found later that the oxidizing action of the ferric chloride was greatest in slightly acid solution and that it was decreased by the addition of strong hydrochloric acid. Solutions made up by dissolving the aniline hydrochloride in a mixture of three parts concentrated hydrochloric acid to one part of water, and adding the ferric chloride, could be boiled with little or no formation of the precipitate.

¹ Jegel, B., *Jahresbericht Chem. technologie*, 1875, 955.

In the work on orthotoluidine hydrochloride it was found that the oxidizing action of the ferric chloride could not be prevented by increasing the amount of acid in the solution. Even solutions which had been saturated with hydrochloric acid gas decomposed on heating.

Ladenburg¹ describes the product formed by the action of ferric chloride on orthotoluidine hydrochloride as the blue dye—toluidine blue—which separates as a flocculent precipitate. It is colored green by hydrochloric acid. The paratoluidine hydrochloride does not form such a compound. These results were confirmed in this work.

This behavior of orthotoluidine hydrochloride led to some qualitative experiments as to the relative ease and rate of oxidation of aniline hydrochloride, of orthotoluidine hydrochloride, of metatoluidine hydrochloride and of paratoluidine hydrochloride by ferric chloride. The results are here given :

Feb. 13, 3 P. M.—0.398 gram aniline hydrochloride was dissolved in 8 cc. of hydrochloric acid, sp. gr. (about) 1.12. To it was added 0.5 gram ferric chloride when the solution was set aside at the ordinary temperature.

Feb. 14, 11 A. M.—The solution had changed color only slightly to a light yellowish green.

Feb. 15, 10.30 A. M.—The solution had become a darker green in color and a slight amount of a greenish precipitate had separated.

Feb. 17, 10 A. M.—The solution had become still darker and contained the green precipitate in quite large amount.

3 P. M.—The solution had separated into two layers, one, about two-thirds of the volume, was dark green and was filled with the precipitate ; the other was a clear greenish yellow liquid.

Feb. 13, 3 P. M.—0.442 grams of orthotoluidine hydrochloride was dissolved in 8 cc. of hydrochloric acid, sp. gr. 1.12 (about) ; 0.5 gram of ferric chloride was added, and the solution was set aside at the ordinary temperature.

Feb. 14, 11 A. M.—The solution had become dark greenish black in color and opaque. This was due to a green precipi-

¹ Ber. d. chem. Ges., 1877, 1127.

tate which had formed ; in thin layers the clear liquid had very nearly the same color as a solution of ferric chloride of the same strength.

Feb. 15, 10.30 A. M.—The color of the solution had not changed very much, but more of the precipitate had formed. The amount being about twice that in the solution the day before.

Feb. 17, 3 P. M.—The solution in thin layers had a brownish-yellow color, and the precipitate was distributed as a light flaky green substance through nearly the whole solution.

Feb. 13, 3 P. M.—0.442 gram metatoluidine hydrochloride was dissolved in 8 cc. hydrochloric acid, sp. gr. (about) 1.12; 0.5 gram ferric chloride was added and the solution set aside at the ordinary temperature.

Feb. 14, 11 A. M.—The solution was dark greenish-black in color, very much like the solution with orthotoluidine hydrochloride. In thin layers the color is more like that of the solution of aniline hydrochloride—a greenish-yellow. There was only a slight precipitate in a very fine state, not like that from the orthotoluidine hydrochloride.

Feb. 15, 10.30 A. M.—More of the precipitate had separated, but the amount was still not very large.

Feb. 17, 3 P. M.—The solution in thin layers had about the same color as the solution of the orthotoluidine hydrochloride. The amount of the precipitate was not so great as in that case.

Feb. 13, 3 P. M.—0.442 gram of paratoluidine hydrochloride was dissolved in 8 cc. of hydrochloric acid, sp. gr. (about) 1.12 ; 0.5 gram of ferric chloride was added and the solution was set aside at the ordinary temperature.

Feb. 14, 11 A. M.—The solution was clear, but the color had changed to a yellowish-red, as seen in thick layers. In thin layers it has a brownish-yellow color.

Feb. 15, 10.30 A. M.—The solution was clear, but the color had become somewhat darker.

Feb. 17, 3 P. M.—No change could be detected in the solution since the last observation.

After some days crystals separated in large plates, but there was no oxidation of the paratoluidine hydrochloride.

From this it is seen that the orthotoluidine hydrochloride is the most readily acted on by the ferric chloride; the metatoluidine hydrochloride comes next; the aniline hydrochloride is less easily attacked, while the paratoluidine hydrochloride is not acted on, as will also be seen in later work.

COMPOUNDS DESCRIBED.

$\text{FeCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$. Dianiline chlorferrate.

$\text{FeCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + \text{H}_2\text{O}$. Hydrous dianiline chlorferrate.

$\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$. Hexaniline chlorferrate.

$\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + 2\text{H}_2\text{O}$. Hydrous hexaniline chlorferrate.

$o\text{-FeCl}_3 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$ + $3\text{H}_2\text{O}$. Hexaorthotoluidine chlorferrate.

$m\text{-FeCl}_3 \cdot 2\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$. Dimetatoluidine chlorferrate.

$m\text{-FeCl}_3 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$. Trimetatoluidine chlorferrate.

$p\text{-FeCl}_3 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$. Triparatoluidine chlorferrate.

$\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + 2\text{H}_2\text{O}$. Dianiline chlorferrite.

$o\text{-FeCl}_2 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$ + $8\text{H}_2\text{O}$. (?) Triorthotoluidine chlorferrite.

$o\text{-FeCl}_2 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$. Hexaorthotoluidine chlorferrite.

$o\text{-FeCl}_2 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$ + $4\text{H}_2\text{O}$. Hydrous hexaorthotoluidine chlorferrite.

To purify the salts for analysis they were filtered off with the aid of the pump, pressed between filter paper to dryness, and the last of the hydrochloric acid was extracted by letting them stand in a desiccator over sulphuric acid and solid potassium hydroxide. This method slightly modified was used by Neumann,¹ who found the same difficulties in his analyses that I found.

The analytical results were often not so close to the values

¹ Ann. Chem. 244, 33.

required by the theory for the corresponding salt, as was desired ; but this was due to the method of formation and to the properties of the salts. They are all decomposed by water and can be recrystallized only from concentrated hydrochloric acid. Some of the salts are decomposed even by the concentrated acid ; the hydrochloride of the organic base separating alone from the solution on cooling.

Dianiline Chlorferrate, $\text{FeCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.

Solutions of ferric chloride and aniline hydrochloride in the ratios of 2 molecules of the former to one of the latter, of 3 : 1, of 4 : 1, and of 8 : 1, give this salt. The solutions 2 : 1 and 3 : 1 may give ; first, the hexaniline chlorferrate, and then—on further concentration—a crop of this salt.

Solution in the Ratio of 2 : 1.—A solution was made by adding to 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, about 50 cc. of hydrochloric acid *i. e.*, nearly three parts of the concentrated acid to one part of water, and dissolving in it 2.4 grams of aniline hydrochloride. After evaporating for some time on the sand-bath and cooling, no crystals separated. The solution was evaporated further and allowed to stand four days over sulphuric acid, when a crop of crystals separated as long thick needles. These crystals in mass had a dark green color ; the dry powder was a lighter green in color. This sample was analyzed. No water was given off on heating the salt.

Solution in the Ratio of 3 : 1.—A solution in this ratio gave on cooling a crop of the hexaniline chlorferrate. The mother-liquor on standing over sulphuric acid for a week gave a crop of long thick needles, which after drying, appeared to be the same green salt obtained from solution 2 : 1. Not enough of the salt was obtained for analysis.

Solution in the Ratio of 4 : 1.—A solution was made by adding 2.4 grams of aniline hydrochloride to 32 cc. of a solution of ferric chloride, containing 12 grams of ferric chloride, and diluting slightly with hydrochloric acid. There was some action of the ferric chloride on the aniline hydrochloride in

this case, as the solution was more dilute than the others. The green precipitate formed was filtered off through glass wool, and the solution was cooled, but no salt separated. After further concentration crystals separated on cooling as long plates of 1-2 cm. in length. They had a resinous brown color; the dry powder was green. On standing over sulphuric acid a second crop of crystals, which looked black in solution, separated. On drying they were found to be long thin brownish green plates. There was also a crop of ferrous chloride.

The analysis of this second crop and of the salt from solution 2 : 1 gave the following results :

	Calculated for $\text{FeCl}_2\cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Found. Salt from solution.	
		4 : 1	2 : 1
Chlorine	42.04	41.87	41.85
		42.07	42.95
Iron	13.30	13.06	
		13.36	13.34

This salt seemed to change its crystalline form according to the conditions of formation. When it was obtained by cooling a hot concentrated solution the plates separated with the brown color. By slow evaporation of the solution over sulphuric acid, the salt was deposited in needles or prisms. The salt is very soluble in weak hydrochloric acid and in water. Some specimens also showed a tendency to take up water on standing.

Hydrous Dianiline Chlorferrate, $\text{FeCl}_2\cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + \text{H}_2\text{O}$.

A solution in the ratio of 4 : 1 was prepared by adding 18 cc. of concentrated hydrochloric acid to 32 cc. of a solution of ferric chloride, which contained 12 grams of ferric chloride, and dissolving in this 2.4 grams of aniline hydrochloride. It was heated on the sand-bath and then cooled, but no salt separated. The solution was then evaporated until a drop cooled on the stirring rod gave crystals. From the solution, which had been left over night to cool, a crop of crystals had separated. They were in the form of long thin needles,

which in solution looked black, but on drying they were of a green color. 2.7 grams of the salt were obtained.

The results of the analysis are the following :

	Calculated for $\text{FeCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} \cdot \text{H}_2\text{O}$.	Found.
Chlorine	40.32	40.26
Iron	12.75	12.60

There was obtained an indication that a still lower compound of ferric chloride and aniline hydrochloride may exist. Near the end of the investigation, *i. e.*, about a year later than the above work, some attempts were being made to obtain other samples of the hydrous dianiline chlorferrate.

A solution was prepared in the ratio of 8 : 1, containing 12 grams of ferric chloride and 1.2 grams of aniline hydrochloride in 35 cc. of concentrated hydrochloric acid. This was boiled on the sand-bath for about an hour, when the character of the solution had changed; on cooling a portion on a glass rod, it no longer wet the rod uniformly, but collected in drops. This solution on cooling gave a crop of short dark red needles forming in compact bunches. The solution was left over sulphuric acid to increase the yield of the compound; but by a sudden change in the weather the solution became heated and the compound dissolved. When again cooled the solution separated a crop of the dianiline chlorferrate in thin green needles of 2 cm. in length.

These gave off a little water on heating at 100°C ., but on analysis for the chlorine, they were found to contain 41.90 per cent., which corresponds to the anhydrous dianiline chlorferrate.

Some further attempts were made to obtain these red needles, and one solution gave a very few of them on cooling; but the solution seemed to be supersaturated, for on stirring it, a large amount of the dianiline chlorferrate separated in plates.

Lack of time prevented further work in this direction.

Hexaniline Chlorferrate, $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.

The preliminary work on this salt was entirely unsuc-

cessful, owing to the oxidation of the aniline hydrochloride, as above mentioned. The salt can be obtained only from strongly acid solutions. It is a beautifully crystalline salt of an orange color, though the color changes with the crystalline habit: and this is dependent on the conditions. This was seen, also, in the case of the dianiline chlorferrate. It is obtained from some solutions in yellow silky needles, either parallel or radiating from a point. By slow cooling or by evaporation over sulphuric acid, it is formed in prisms or heavy needles crystallizing in bunches, where the crystals cross each other in the middle, giving a very beautiful specimen.

The salt is very soluble in water, alcohol and dilute acids; but it is decomposed at the same time, since the ferric chloride oxidizes the aniline hydrochloride to form the blue precipitate previously described. The solutions of the salt in hydrochloric acid, sp. gr. about 1.12, range from a light yellow color in dilute solutions, to a blackish-green color in concentrated solutions which have stood a short time. When the salt is dropped into a solution of sodium hydroxide, or better when such a solution is added to a solution of the salt in dilute hydrochloric acid, the aniline is set free and collects in drops on the surface, and the iron is precipitated as red ferric hydroxide. The dianiline chlorferrate acts similarly and the solutions of both salts give all the tests for ferric iron.

This salt was obtained from solutions of ferric chloride and aniline hydrochloride in all the ratios of 3 : 1; 2 : 1; 1 : 1; 1 : 2; 1 : 3; 1 : 4; and 1 : 8. In the solutions 3 : 1 and 2 : 1 either this or the dianiline chlorferrate may separate; or first, a crop of the hexaniline chlorferrate may separate and then, from the mother-liquor a crop of the dianiline salt may be deposited, as above described.

Solution in the Ratio of 3 : 1.—24 cc. of a solution of ferric chloride, containing 9 grams of ferric chloride, was diluted with 10 cc. of concentrated hydrochloric acid, and in it was dissolved 2.4 grams of aniline hydrochloride. The solution was heated on the sand-bath to boiling; but on cooling no salt

separated. It was then further evaporated until a drop of the liquid, cooled on a glass rod, gave crystals. After standing over night, the solution contained a bunch of long yellow needles that nearly half filled the liquid.

Another solution in the ratio of 3 : 1 was made, which contained 6 grams of ferric chloride and 1.6 grams of aniline hydrochloride. A crop of yellow fine silky needles was deposited from the solution.

Both of these salts were analyzed with the following results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	First preparation. Found.	Second preparation. Found.
Chlorine	33.94	34.38	35.27
Iron	5.96	6.47	6.48

Solution in the Ratio of 2 : 1.—16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, was added to 18 cc. of concentrated hydrochloric acid, and in this was dissolved 2.4 grams aniline hydrochloride. On cooling this solution, a crop of fine silky crystals of a brownish-yellow color separated. 1.5 grams of the salt were obtained.

Solution in the Ratio of 1 : 1.—A solution was made by mixing 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, with 18 cc. of concentrated hydrochloric acid and adding 4.8 grams of aniline hydrochloride. From this solution 3.1 grams of a salt was obtained in the form of fine silky needles, which in the solution had a golden-yellow color. The results of the analyses of these salts were the following :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Found. Solution 2 : 1.	Salt from Solution 1 : 1.
Chlorine	33.94	33.44	33.48
Iron	5.96	6.38	6.10

There was no water given off on heating the salt from solution 2 : 1 ; the salt from solution 1 : 1 was not tested.

Solution in the Ratio of 1 : 2.—A solution of 16 cc. of ferric chloride, equal to 6 grams of ferric chloride, was added to 20 cc. of concentrated hydrochloric acid, and 9.6 grams of aniline hydrochloride was dissolved in it. It was difficult to dis-

solve all of the aniline hydrochloride ; so the solution was further diluted to keep all the double salt dissolved. 6.47 grams of the salt separated, on cooling, in larger needles than those obtained from the preceding solutions. They were also of a darker yellow color when in the solution, and when dried they had a brownish tint.

Solution in the Ratio of 1 : 4.—A solution containing 3 grams of ferric chloride and 9.5 grams of aniline hydrochloride was made up with hydrochloric acid to a volume of 50 cc. The solution at first was evaporated too far, so that on cooling it became nearly solid with the salt. It was, therefore, diluted with strong hydrochloric acid and heated ; on cooling the salt separated in yellow needles. The analyses of these salts give the following results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Found for salt from Solution 1 : 2.	Found for salt from Solution 1 : 4.
Chlorine	33.94	34.64	33.45 33.50
Iron	5.96	5.61	6.03 6.19

The salt was best obtained from a solution in the ratio of 1 : 4, as follows : 11.6 cc. of a solution of ferric chloride, containing 3 grams of ferric chloride, was diluted to 75 cc. with hydrochloric acid—three parts of concentrated acid to one part water—and in it were dissolved 9.4 grams of aniline hydrochloride. The solution was heated on a water-bath, when it became a deep brownish-red in color and remained perfectly clear. The salt crystallized in needles and prisms, which had a yellow color when viewed on the side, but when viewed on the ends they showed a decided red color. The dry salt in coarse powder had a reddish-yellow color, but in fine powder it was a pure yellow. Six grams of the crystals were obtained.

Another preparation of the salt was made just as above. Part of the salt was dried and prepared for analysis ; a second part was recrystallized from concentrated hydrochloric acid. The recrystallized salt formed, like that from the first 1 : 4 solution, in needles crossing each other in the middle. The

mother-liquor from this specimen, on standing over sulphuric acid, separated a crop of single needles starting at the surface of the liquid and extending down through the solution.

The three portions gave these results on analysis :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Uncrystallized.	Found. Recrystallized.	
Chlorine	33.94	33.39 33.80	1st crop. 33.76	2d crop. 33.83
Iron	5.96	{ 6.09 6.29	6.12	
Nitrogen	8.95	{ 8.41 8.45		
		No water given off on heating.	No water given off on heating.	

The nitrogen determinations were made by Mr. W. A. Jones of this laboratory, to whom I here express my thanks.

Solution in the Ratio of 1 : 8.—A solution was prepared containing 3 grams of ferric chloride and 19.1 grams of aniline hydrochloride. The salt separated in yellow crystals as fine needles and in prisms which frayed off on the ends into long fine needles. These prisms cross in the middle.

The results of the analyses were the following :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Found.
Chlorine	33.94	33.64 33.78
Iron	5.96	5.94 5.90

The salt gave off no water on heating to 100° .

Very fine specimens of the hexaniline chlorferrate were obtained from solutions of ferrous chloride and aniline hydrochloride during the work on the salts formed by the action of ferrous chloride on aniline hydrochloride. On exposure to the air the ferrous chloride became oxidized to ferric chloride which in the presence of excess of aniline hydrochloride formed the higher salt. In one case a specimen of the *dianiline* chlorferrate was obtained. The addition of a little hydrogen peroxide to the solution of the ferrous compounds also produced the hexaniline chlorferrate.

The crystalline form of the salt obtained thus was the same as when obtained from ferric chloride directly.

Analyses of some samples obtained thus, gave the following results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$.	I.	Found. II.	III.
Chlorine	33.94	33.83 33.68	33.44 33.44	33.60 33.50
Iron	5.96	6.49	6.19 6.23	6.66 6.46

Hydrous Hexaniline Chlorferrate, $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_3\text{Cl} + 2\text{H}_2\text{O}$.

A solution of ferrous chloride and aniline hydrochloride in the ratio 2 : 1 had stood in contact with the air until it contained a large quantity of the orange *ferric* salt, the hexaniline chlorferrate. This was filtered off and recrystallized from concentrated hydrochloric acid.

On analysis it gave the following results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_3\text{Cl} \cdot 2\text{H}_2\text{O}$.	Found.
Iron	32.70	32.73 32.80
Chlorine	5.74	5.78 5.82

No attempt was made to determine the water of crystallization, as the method had not been worked out at that time.

A second crop from the mother-liquor gave analyses for the anhydrous salt. The results are given under the hexaniline chlorferrates, from ferrous chloride and aniline hydrochloride No. I. An attempt was made to obtain the hydrous salt by recrystallizing the hexaniline chlorferrate, obtained from a solution of ferric chloride and aniline hydrochloride, from concentrated hydrochloric acid, but the *anhydrous* salt was obtained.

Hexaorthotoluidine Chlorferrate, $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \cdot 3\text{H}_2\text{O}$.

The first attempts to obtain double salts with ferric chloride and orthotoluidine hydrochloride were not satisfactory, owing to the oxidation of the toluidine hydrochloride by the ferric chloride.

A solution of ferric chloride and orthotoluidine hydrochloride in hydrochloric acid, part dilute acid, and part concentrated acid, was made in the ratio of 1 : 1. It was heated to boiling, when a dark tarry oil separated and fell to the bottom of the beaker. The solution was evaporated to about one-half and cooled, when a crystalline substance separated. This was not investigated to any great extent. The mother-liquor, on standing over sulphuric acid, gave a crop of crystals in the form of needles having a brownish-yellow color, and crystallizing in clusters. About one gram of the salt was obtained, which was analyzed.

Another solution in the ratio of 1 : 1, and a solution in the ratio of 2 : 1 were prepared. From these, however, only a slight amount of the double salt was obtained, mixed with tarry decomposition products. Ferrous chloride was also deposited. Most of the action in both solutions was the oxidation of the *o*-toluidine hydrochloride.

A solution, nearly in ratio of 1 : 1, was made from 17 cc. of a solution of ferric chloride, containing 6.4 grams ferric chloride, and 5.27 grams of *o*-toluidine hydrochloride in 34 cc. of dilute hydrochloric acid and 10 cc. of the concentrated acid. The solution, on heating, became first colored deep red, then quite black, and began to decompose. It was boiled about two hours, filtered, and cooled; after about one and a half hours a crop of a salt separated. The salt formed a bunch of needles, which started to crystallize at a point on the side of the beaker, and nearly filled the solution. 3.47 grams of the reddish-yellow salt were obtained.

Another solution in the ratio of 1 : 1, using 6 grams of ferric chloride and 5.27 grams of *o*-toluidine hydrochloride was made up with 10 cc. of dilute acid and 5 cc. of the concentrated acid. The solution was heated to boiling for about half an hour, when there was a slight oxidation of the *o*-toluidine hydrochloride. After filtering the hot solution and letting it cool the salt filled the solution so that the beaker could be turned up-side-down without spilling the liquid. 4.42 grams of the salt were obtained. On drying between filter paper in

the press the edges of these two samples turned to a green color.

Analyses of the samples give the following results :

Calculated for $\text{FeCl}_2 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} + 3\text{H}_2\text{O}$		Found.		
		1st sample.	2nd sample.	3rd sample.
Chlorine	29.59	29.24	30.29	29.12 29.22
Iron	5.20	5.20	5.02 5.34	5.04 5.18

In other solutions in different ratios there was not so much success in the work ; more of the oxidation product was formed.

New Method of Preparation.—It was thought that the double salt might be obtained from solutions of ferric chloride and *o*-toluidine hydrochloride dissolved in dilute hydrochloric acid, sp. gr. 1.12, by saturating the solution with hydrochloric acid gas. This was tried with such success that it was used in all the subsequent work.

By this method the hexaorthotoluidine chlorferrate was obtained from solutions of ferric chloride and *o*-toluidine hydrochloride in ratios of 4 : 1 ; 2 : 1 ; 1 : 1 ; 1 : 4 ; 1 : 8 ; and 1 : 12. The salt could be recrystallized from concentrated hydrochloric acid by saturating the warm acid with the salt, and allowing the solution to cool ; or by nearly saturating weak cold hydrochloric acid with the salt and passing into the solution hydrochloric acid gas nearly to saturation. On trying to recrystallize the salt from dilute acid it was decomposed and toluidine hydrochloride separated. In solution in water and in ethyl alcohol the salt decomposed into its constituents, which then reacted to form the oxidation product. Ethyl ether decomposed the salt, leaving a white solid. The crystals of the salt formed in best shape by slow evaporation of the strong hydrochloric acid solution over sulphuric acid and solid potassium hydroxide.

Solution in the Ratio of 4 : 1.—To 21 cc. of a solution of ferric chloride, containing 8 grams of ferric chloride, 1.77 grams of *o*-toluidine hydrochloride was added. The solution was

prepared cold and allowed to stand about an hour and a half, during which time—the solution not being strongly acid—the substances had reacted so that the solution became green. —This shows the ease with which ferric chloride acts on *o*-toluidine hydrochloride.—The beaker containing the solution was placed in cold water while hydrochloric acid gas was allowed to pass into it. After filtering the solution it was allowed to stand over night, when a crop of the salt separated in reddish-yellow needles crystallizing in bunches. 1.04 grams of the salt were obtained.

Solution in the Ratio of 2 : 1.—32 cc. of a solution of ferric chloride, containing 12 grams of ferric chloride, and 5.27 grams of *o*-toluidine hydrochloride gave a salt as an amorphous powder—or in such small crystals that their form was not noticed—when the cold solution was saturated with hydrochloric acid gas. This powder was filtered off and recrystallized by dissolving in hydrochloric acid—one-half concentrated acid to one-half dilute acid—and saturating the solution with hydrochloric acid gas. After standing four days over sulphuric acid, 2.5 grams of the needles were obtained.

Solution in the Ratio of 1 : 1.—To 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, 5.27 grams of *o*-toluidine hydrochloride were added, which did not all dissolve. The solution was nearly saturated with the hydrochloric acid gas. It became heated on absorbing the gas so that on cooling the salt separated in good condition.

The results of the analyses of these salts were the following :

Calculated for		Found for salt from		
$o\text{-FeCl}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\text{Cl}\cdot 3\text{H}_2\text{O}$		Sol. 4 : 1.	Sol. 2 : 1.	Sol. 1 : 1.
Chlorine	29.59	29.69	29.33	29.41
		29.69	29.31	29.43
Iron	5.20	5.76	5.42	5.83
		5.47	5.19	

Solution in the Ratio of 1 : 4.—To 20 cc. of hydrochloric acid—1 part dilute acid to 1 part concentrated acid—1 gram of ferric chloride and 3.536 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the

solution became nearly solid with the salt which separated. The salt was filtered off and as much of the liquid as possible was separated by use of the filter pump. The salt was divided into three parts: Part I was prepared for analysis without recrystallization; part II was recrystallized by saturating hot concentrated acid with the salt and cooling; part III was recrystallized by dissolving in the dilute acid and saturating the solution with the gas. There was not enough of the salt, from part II, obtained for the determination of both iron and chlorine. The results of the analysis are as follows:

	Calculated for $\alpha\text{-FeCl}_3 \cdot 6\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \text{Cl}_3\text{H}_3\text{O}$	Part I.	Found. Part II.	Part III.
Chlorine	29.59	29.52	29.49	29.76
Iron	5.20	5.12		5.64

Solution in the ratio of 1 : 8.—2.7 cc. of a solution of ferric chloride—containing 1 gram of ferric chloride—was diluted to about 35 cc. with hydrochloric acid and 7.07 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the solution became nearly solid from the separation of the salt. About two-thirds of this solid mass was heated to 40° with 75 cc. of concentrated hydrochloric acid; on cooling *o*-toluidine hydrochloride separated. This was filtered off and from the filtrate the reddish-yellow needles were obtained.

Solution in the ratio of 1 : 12.—1 gram of ferric chloride in solution and 10.609 grams of *o*-toluidine hydrochloride were dissolved in 40 cc. of concentrated hydrochloric acid. The solution was cooled and hydrochloric acid gas passed in, when on standing over night both *o*-toluidine hydrochloride and the double salt crystallized out. By fractional crystallization the double salt was obtained pure.

The analyses of these samples give these results:

	Calculated for $\alpha\text{-FeCl}_3 \cdot 6\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \text{Cl}_3\text{H}_3\text{O}$	Found for salt from Sol. 1 : 8.	Sol. 1 : 12.
Chlorine	29.59	29.60	29.69
Iron	5.20	5.65	

A sample of the salt from the solution 1 : 8 was heated at

95–100° C., when it gave off water. When heated to 125° it was found that *o*-toluidine had sublimed.

The hexaorthotoluidine chlorferrate was obtained also, by oxidation of solutions of ferrous chloride and *o*-toluidine hydrochloride on exposure to the air. When it was attempted to obtain second crops of crystals from solutions of the ferrous chloride and toluidine hydrochloride the *ferric* double salt separated. Two samples of second crops of crystals from solutions of ferrous chloride and *o*-toluidine hydrochloride in the ratios 2 : 1 and 3 : 1 gave on analysis the following results :

	Calculated for $o\text{-FeCl}_3 \cdot 6\text{C}_6\text{H}_4 \text{ } \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \cdot 3\text{H}_2\text{O}$	Found for salt from Sol. 2 : 1.	Found for salt from Sol. 3 : 1.
Chlorine	29.59	29.25	29.36
Iron	5.20	5.95	5.35

Many attempts were made to prepare double chlorides of ferric chloride and *o*-toluidine hydrochloride containing a larger proportion of ferric chloride ; but without success. Solutions in the ratio of 8 molecules of ferric chloride to 1 molecule of *o*-toluidine hydrochloride were made from 21 cc. of a solution of ferric chloride—containing 8 grams of ferric chloride—and 0.884 grams of dry *o*-toluidine hydrochloride. When these solutions were saturated in the cold, with the gaseous hydrochloric acid, a little of a salt, that seemed to be the hexaorthotoluidine chlorferrate, separated, but quickly dissolved. No salt could then be obtained from the solution even on cooling in ice-water. On heating the solutions in order to concentrate them, the *o*-toluidine hydrochloride was destroyed, no matter how acid the solution had been made.

Attempts were also made to obtain a salt from a very nearly saturated solution of ferric chloride containing 8 grams of ferric chloride, to which was added 0.884 gram of *o*-toluidine hydrochloride, by saturating with the gaseous acid, and cooling in ice-water ; but without success.



This salt separated from concentrated solutions of ferric chloride and *m*-toluidine hydrochloride in the ratio of four molecules

of ferric chloride to one molecule of *m*-toluidine hydrochloride, 3 : 1 ; 2 : 1 ; 1 : 4 and 1 : 6, in shining yellow plates when the gaseous hydrochloric acid was passed into the solution. The salt was deliquescent and could not always be obtained in condition for analysis.

Solution in the ratio of 1 : 1.—A solution of ferric chloride, containing 1 gram of ferric chloride, was diluted up to 15 cc. with hydrochloric acid, sp. gr. 1.12, and 0.881 gram of *m*-toluidine hydrochloride added. The toluidine hydrochloride dissolved on heating and the solution became dark colored. It was then cooled to 27° and saturated at that temperature with hydrochloric acid gas, when drops of a dark oil separated, but no salt. The beaker was then placed in crushed ice and the gas passed in to saturation. Some crystals of a salt separated in plates, but they could not be obtained, as they dissolved on taking the solution out of the ice-water.

The ratio of the solution was changed to 2 : 1 by the addition of 1.55 cc. of a solution of ferric chloride containing 1 gram of ferric chloride. From this no salt was obtained.

The ratio of this solution was again changed to 3 : 1 by the addition of 1.55 cc. of the ferric chloride solution. The liquid was cooled in ice-water and again saturated with hydrochloric acid gas, but no salt was obtained. The volume had thus been increased to 20 cc. and must have been too dilute, as subsequent work showed.

A second solution in the ratio of 1 : 1 was prepared like the first, except that the volume was only 10 cc. It, also, became dark colored on heating. When the hydrochloric acid gas was passed into the hot solution the oily liquid separated and the color became lighter. On cooling the solution in cold water and passing in the acid gas, nothing separated until the liquid was stirred ; then it became filled with yellow plates, which were taken for *m*-toluidine hydrochloride in the yellow solution.—They were no doubt the dimetatoluidine chlorferrate.—The ratio was now changed to 2 : 1 as before, but from this solution the yellow plates separated. On dry-

ing, the salt had a dark green color in mass, but a lighter green color when powdered. It gives reactions for iron in the ferric state, and for toluidine.—The green color may have been due to the presence of some decomposition-product of the toluidine hydrochloride.—A third solution in the ratio of 1 : 1 was made just like the second 1 : 1 solution, but the *m*-toluidine hydrochloride was dissolved in the acid and this was cooled ; then the ferric chloride was added. Hydrochloric acid gas was passed into the solution at about 15°, when some of the yellow plates separated. It was then cooled in ice-water and saturated with the gas. There was no oxidation of the *m*-toluidine hydrochloride in this case. The salt was filtered off, pressed and dried. The yellow plates when dry gave a yellow powder. The salt was analyzed.

Solution in the ratio of 1 : 4.—A solution was prepared containing 0.5 gram of ferric chloride and 1.762 gram of *m*-toluidine hydrochloride in 8 cc. of liquid. On passing in hydrochloric acid gas a few plates separated, but the solution became warm. It was therefore cooled in ice-water, when the oil separated in a cloud, but by the continued action of the gas, the solution cleared up and the salt separated in shining yellow plates. The salt was deliquescent.

The mother-liquors from these two salts were mixed when more of the salts separated. This was also deliquescent. It was dried over caustic potash until no odor of hydrochloric acid was detected on it ; then on heating to 105–110° no water was given off, although toluidine hydrochloride sublimed.

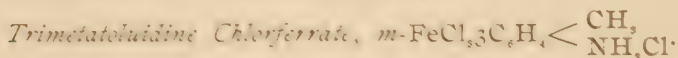
Solution in the ratio of 4 : 1.—A solution was prepared containing 4 grams of ferric chloride and 0.881 gram of *m*-toluidine hydrochloride, which had a volume of 10 cc. The solution, which was cooled in ice-water, when saturated with hydrochloric acid gas, deposited first the oil, then it cleared and the salt formed. It looked like the salt previously obtained.

The analyses of these salts gave the following results:

	Calculated for $m\text{-FeCl}_3 \cdot 2\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{NH}_2\text{Cl} \end{smallmatrix}$		Found for salt from.	
		sol. 1:1.	sol. 1:4.	sol. 4:1.
Chlorine	39.42	38.75	38.74	38.40
Iron	12.47	12.31	12.46	12.90

Dimetatoluidine Chlorferrate.

Solution in the ratio of 8 : 1.—A solution was made by adding 0.881 gram of *m*-toluidine hydrochloride to 12.4 cc. of a solution of ferric chloride, containing 8 grams of ferric chloride. The substance began to react at ordinary temperatures; a dark blackish oil separated. The solution was placed in ice-water and saturated with hydrochloric acid gas, when the oil solidified. This solid looked like the dimetatoluidine chlorferrate from the 1:4 solution. On removing the solution from the ice-water, most of the salt dissolved, so that it could not be obtained in condition for analysis.



This salt could not be obtained in very satisfactory condition; only one specimen was obtained pure enough for analysis. When solutions in the ratios of 1 : 3; 1 : 4 and 1 : 6 were saturated with hydrochloric acid gas, first the lower salt separated; but, on continued action of the acid, the lower salt changed its crystalline form and the higher salt was produced.

Solution in the ratio of 1 : 3.—To a solution of 2.643 grams of *m*-toluidine hydrochloride in 6.2 cc. of dilute hydrochloric acid was added 3.88 cc. of a solution of ferric chloride containing 1 gram of ferric chloride. The beaker containing the solution was placed in cold water and hydrochloric acid gas was passed into it. When the oil separated the beaker was placed in crushed ice while the saturation with the gaseous acid continued. The solution cleared up and then crystals separated into two forms: all through the solution were yellow plates as in solution 1 : 4, then there were bunches of crystals that looked green. These were all broken up with the stirring rod and 2.5 cc. of dilute hydrochloric acid were added. On continued absorption of hydrochloric acid gas the crystals changed form and the yellow plates were replaced by finer

crystals of a lighter yellow color. When the change seemed to be complete, the mass—which looked like hexaorthotoluidine chlorferrate as it separated from concentrated solution—was filtered off.

The salt formed a sticky mass fuming with hydrochloric acid. It was very difficult to prepare for analysis, being deliquescent in the air and adhering to the drying-paper. The salt which was left, part of it having been dissolved by the moisture of the air and absorbed by the drying-paper, was further dried in a desiccator.

Part of the salt before the final drying was dissolved in hot concentrated hydrochloric acid and the solution was cooled in ice-water. The salt which separated was the dimetatoluidine chlorferrate.

The analyses of the dried salt gave the following results :

Chlorine	35.61
Iron	10.17

The ratio of the iron to the chlorine in the salt was 1 : 5.54. Taking the ratio as 1 : 6 the salt must have been the trimetatoluidine chlorferrate, for which the calculated percentages are chlorine 35.85, and iron 9.45.

A second solution in the ratio of 1 : 3 was prepared which contained the same amounts of toluidine hydrochloride and of ferric chloride, but whose volume was 15 cc. This gave first the dimetatoluidine chlorferrate. The continued action of the hydrochloric acid gas produced the same change as before, but the substance which separated seemed to be a mixture of the two salts.

The ratio of the constituents was changed to 1 : 6 by the addition of 2.643 grams of the toluidine hydrochloride in 9 cc. of hydrochloric acid. The solution was warmed to bring all the salts into solution. When it had been cooled and hydrochloric acid gas passed into it, the dimetatoluidine chlorferrate separated without the formation of the oil. This salt did not change over to the higher salt so far as could be seen. When the beaker was removed from the ice-water most of the

salt was dissolved. The difficulty may have been the greater dilution of the solution.

A second solution in ratio of 1 : 6 was prepared containing 0.5 gram of ferric chloride and 2.643 grams of *m*-toluidine hydrochloride in 10 cc. of liquid. The dimetatoluidine salt separated first, then some of the lighter fine crystals appeared, which seemed to be composed of fine needles. After one to two hours the whole of the crystals seemed to have changed over to this form.

All attempts to get this crop of crystals in condition for analysis failed. The mother-liquor could not be entirely separated by the use of the filter-pump, and the solution was so strongly acid that the drying-paper was disintegrated and mixed with the salt, so that they could not be separated. No further attempts to prepare this salt were made.

Triparatoluidine Chlorferrate, $p\text{-FeCl}_3 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$.

The first part of the work with ferric chloride and *p*-toluidine hydrochloride was very unsatisfactory—as was the preliminary work on the other double chlorides. Many samples of the salts were prepared and analyzed only to find that the composition was not constant, the samples were mixtures. This could be discovered only after the analyses were finished; as all attempts to recrystallize the salts resulted in breaking them down into their constituents. Solutions were made in the ratio of 1 : 1 and 1 : 4. From solutions in ratio 1 : 4 only *p*-toluidine hydrochloride separated. From the solutions in the ratio 1 : 1 a salt was obtained in good shape; but on standing over sulphuric acid to concentrate the solution, the salt broke down into its constituents.

It was thought from some previous work on ferrous chloride with *o*-toluidine hydrochloride that the union of the two chlorides might be facilitated by keeping the solution at the boiling temperature for a long time, but this preliminary work showed that this did not hold, for ferric chloride and *p*-toluidine hydrochloride. This work showed, also, that the double salt cannot exist except in strongly acid solution, and

that the ferric chloride acts on the *p*-toluidine hydrochloride much less than it does on the ortho- and on the metatoluidine hydrochloride.

The triparatoluidine chlorferrate was obtained from solutions of ferric chloride and *p*-toluidine hydrochloride in ratios of two molecules of ferric chloride to one of *p*-toluidine hydrochloride, of 3 : 1 and of 6 : 1. The salt separated from the solutions in glancing red crystals whose form changed somewhat with the conditions of its preparation. In some cases it was obtained in plates, in other cases as thick prisms.

Solution in the ratio of 2 : 1.—0.881 gram of *p*-toluidine hydrochloride was dissolved in 15 cc. of dilute hydrochloric acid and 3.1 cc. of a solution of ferric chloride, containing 2 grams of ferric chloride, were added. The warm solution was treated with hydrochloric acid gas, when *p*-toluidine hydrochloride separated. It was then placed in ice-water and the gas passed through the solution, but the salt did not separate. Thinking that the temperature might be too low, the solution was heated and the gaseous acid was passed in while the solution cooled. A double salt separated, but *p*-toluidine hydrochloride was mixed with it. From the mother-liquor a double salt separated in short prisms with glancing faces. As they were free from *p*-toluidine hydrochloride they were prepared for analysis.

Triparatoluidine Chlorferrate.

Solution in the ratio of 3 : 1.—A solution was prepared containing 6 grams of ferric chloride and 1.76 grams of *p*-toluidine hydrochloride in 40 cc. of dilute hydrochloric acid. The solution was heated to boiling and the hot, nearly opaque, red solution was treated with hydrochloric acid gas until it was strongly acid. It was then cooled and more of the gas passed into it. The absorption of the gas produced much heat. At first *p*-toluidine hydrochloride separated; this was then changed to the double salt. The salt was filtered off, when it was seen to be composed of reddish-yellow plates. In fine powder the salt was of a darker color than were some of the specimens previously obtained.

The analyses of these salts gave the following results :

	Calculated for $p\text{-FeCl}_3 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$	Found for salt from	
		Sol. 2 : 1.	Sol. 3 : 1.
Chlorine	35.85	35.55	35.60
Iron	9.45	9.27	9.43
Nitrogen	7.04		6.80
Water	0.0		0.0

The salt from solution 3 : 1 on heating at $110\text{--}115^\circ$ gave off no water, but a sublimate of toluidine hydrochloride was formed. The determination of the nitrogen was made by Mr. Van Clieve, of this laboratory, to whom I express my thanks.

Solutions in the ratio of 6 : 1.—0.881 gram of *p*-toluidine hydrochloride was added to 9.3 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride. The solution was warmed slightly and hydrochloric acid gas was passed into it, when it became hot. The beaker was then placed in cold water while the saturation with the hydrochloric acid gas was continued. The solution was left over night, when a crop of the red salt separated. This was prepared for analysis.

A second solution was made up like the last except that it was diluted with 10 cc. of dilute hydrochloric acid. The solution was saturated with hydrochloric acid gas as it cooled to near zero in ice-water ; when a crop of the salt separated.

The results of the analyses of these samples of the salt were the following :

	Calculated for $\text{FeCl}_3 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2\text{Cl} \end{smallmatrix}$	Found for salt from	
		First sol.	Second sol.
Chlorine	35.85	35.64	36.16
Iron	9.45	9.36	10.01

SALTS FROM FERROUS CHLORIDE.

Salts from Ferrous Chloride and Aniline Hydrochloride.

The work on the ferrous chloride with aniline hydrochloride was carried on simultaneously with that on *ferric chloride* with aniline hydrochloride, before the methods of work were well developed. The first results were not clear ; and much work was done before reliable results were obtained. From this preliminary work, however, some important results were

obtained. It was found that solutions of ferrous chloride and aniline hydrochloride in the ratios of 3:1; 2:1; 1:1; 1:2, in slightly acid solutions, gave mixtures of aniline hydrochloride in plates, nearly white or light yellow crystals in short needles, and, often mixed with these, were red crystals in thicker, longer needles than the yellow ones. Then it was found that the solutions, which were filtered hot in contact with the air or which stood for a long time exposed to the air, gave a larger proportion of the red crystals. This led to the conclusion that the red crystals were a compound of ferric iron. A sample of the red crystals, which was obtained free from the light-yellow needles, gave the ordinary reactions for iron in the *ferric* state. When a solution of the salt in dilute hydrochloric acid was tested with potassium ferricyanide, the solution gave only a greenish coloration; with potassium ferrocyanide a dark blue precipitate was formed; and potassium hydroxide or sodium hydroxide gave a red hydroxide of ferric iron, which was not changed by hydrogen peroxide. The salt was analyzed and it proved to be the hexaniline *chlorferrate*.

0.2133 gram salt gave 0.2892 gram AgCl.

0.2035 gram salt gave 0.0198 gram Fe_2O_3 .

The determination of iron was made by fusing the salt with the sodium potassium carbonate without reprecipitation, which gave too high results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$.	Found.
Chlorine	33.94	33.53
Iron	5.96	6.80

The light-yellow needles, when freshly prepared and quickly freed from the mother-liquor, were nearly white; but they became slightly yellow before they could be filtered in quantity from the mother-liquor. They gave all the reactions for iron in the ferrous state. The best test was the formation of the ferrous hydroxide and its instantaneous change to the red ferric hydroxide, when hydrogen peroxide was added.

It was also found that a slightly acid solution of the ferrous chloride and aniline hydrochloride, which had deposited the

aniline hydrochloride, gave a good yield of the light-yellow needles when concentrated hydrochloric acid was poured into the solution. The change of the plates of aniline hydrochloride over to the needles of the double salt wherever the strong acid came in contact with them was very interesting to watch. It was then found that by using quite strongly acid solutions the ferrous double salt could be obtained, on the first cooling of the solution, free from the ferric salt. A sample of the light-yellow crystals on analysis gave results that pointed to the formula $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} \cdot 2\text{H}_2\text{O}$, for the salt.

	Calculated for $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + 2\text{H}_2\text{O}$.	Found.
Chlorine	33.58	33.23 32.89
Iron	13.28	14.44 15.03

Dianiline Chlorferrite, $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} \cdot 2\text{H}_2\text{O}$.

This salt was obtained from solutions containing all proportions of ferrous chloride and aniline hydrochloride, from 1 : 4 to such a ratio that ferrous chloride separated from the solution mixed with the double salt. In a series of experiments four solutions were made up in the ratios 4 : 1 ; 3 : 1 ; 2 : 1 ; and 1 : 1.

Solution in the ratio of 4 : 1.—This solution contained 8.72 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 50 cc. of liquid. It was heated to boiling for a time, but on cooling no salt separated. When it was placed in snow a crop of the light-yellow needles separated. By the next morning a second crop of the salt had formed at the ordinary temperature. The salt was filtered off and prepared for analysis.

Solution in the ratio of 3 : 1.—This solution contained 6.54 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 39 cc. of liquid. The solution was boiled a short time and then cooled, when the light-yellow salt separated at ordinary temperatures. This was filtered off and prepared for analysis. The next morning a second crop of the salt had

formed, but it was mixed with crystals of ferrous chloride.

Solution in the ratio of 2 : 1.—This solution was composed of 4.36 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 29 cc. of liquid. After boiling and cooling, the solution deposited about twice as much of the light-yellow crystals as did the solution "3 : 1." This crop of the salt was prepared for analysis. The second crop of the salt in this case also contained crystals of the ferrous chloride.

Solution in the ratio of 1 : 1.—The solution contained 2.18 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 19 cc. of liquid. The solution was boiled and then allowed to cool, when it became nearly solid with the salt which had separated. The salt was dissolved by the addition of dilute hydrochloric acid and heating; it was then left over night, when there was a crop of the light-yellow crystals mixed with some of the red ferric salt. These were separated mechanically and the ferrous salt was prepared for analysis. The analyses of these crops gave the following results :

	Calculated for $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} \cdot 2\text{H}_2\text{O}$.	Sol. 4 : 1.	Found for salt from		
			Sol. 3 : 1.	Sol. 2 : 1.	Sol. 1 : 1.
Chlorine	33.58	33.75 33.86	33.91 33.76	33.61 33.15	33.66
Iron	13.28	14.12	13.31 13.86	14.16 14.26	

A solution was made in the ratio of 1 : 2.5, which contained 13.68 grams of ferrous chloride and 32.9 grams of aniline hydrochloride in 183 cc. of solution. The solution was only slightly acid; so that on boiling and cooling only aniline hydrochloride separated. About one-half the volume of concentrated hydrochloric acid was added; the solution was then heated and allowed to cool when the light-yellow ferrous salt separated in large quantity. This was filtered off and prepared for analysis, the results of which were as follows :

	Calculated for $\text{FeCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2\text{Cl} \cdot 2\text{H}_2\text{O}$.	Found.
Chlorine	33.58	33.88
Iron	13.28	13.25

From the mother-liquor more of the salt crystallized. This was left in the solution, when after two days the ferric salt appeared all through the mass. After standing some weeks the change to the ferric double salt seemed to be complete. This salt gave on analysis results agreeing with those required for the hexaniline chlorferrate.

The dianiline chlorferrite when heated in the air-bath at 90° turned nearly black and, when this residue was dissolved in water, a dark solution was obtained with some insoluble substance; the salt is therefore decomposed on heating even at 90° C.

When allowed to stand in the sulphuric acid desiccator the salt loses weight, but, as before stated, in treating of the methods of analysis, the percentage of water could not be determined.

The ferrous salts do not keep well. After remaining in the specimen tube a short time—a few weeks—they change color, becoming green and showing other signs of decomposition.

Triorthotoluidine Chlorferrite, $\text{FeCl}_2 \cdot 3\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \cdot \text{Cl} \cdot 6\text{H}_2\text{O}$.

This salt was obtained only once, when the analyses were reliable, though the analyses of another preparation pointed to the same salt with more water of crystallization. In all subsequent work the salt to be described later was obtained.

Three solutions were prepared. The first solution, in the ratio of 1 : 1, was composed of 10 cc. of a saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, and a nearly saturated solution of 4.5 grams of *o*-toluidine hydrochloride. This solution, when heated and then allowed to cool, gave only *o*-toluidine hydrochloride.

The second solution, in the ratio of 2 : 1, was made by mixing 20 cc. of the saturated solution of ferrous chloride with a saturated solution of 4.5 grams of *o*-toluidine hydrochloride. From this there separated, first, ferrous chloride, then a double salt. The double salt was dissolved by warming the solution and pouring off from the crystals of ferrous

chloride. From the liquid there separated a crop of yellow crystals in long fine needles. The analyses of this sample did not give concordant results.

The third solution was composed of 12 grams of ferrous chloride in saturated solution and 4.5 grams of *o*-toluidine hydrochloride in saturated solution. This first gave ferrous chloride, then the mother-liquor gave a mixture of the yellow needles, as obtained in the previous solution, with toluidine hydrochloride and crystals of a different yellow color.

Solution in the ratio of 1 : 1.—As it was thought that these solutions did not contain enough acid, a second solution, in the ratio of 1 : 1, was prepared thus: 10 cc. of the saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, was added to a solution of 4.5 grams of *o*-toluidine hydrochloride in 15 cc. of concentrated hydrochloric acid and 5 cc. of water. The solution was heated, and, when it was cooled, a crop of crystals formed which, when viewed on the ends, had a reddish-yellow color; but, when viewed on the side, were of a light-yellow color. 3 grams of the dry salt were obtained. On analysis the salts gave the following results:

	Calculated for $\text{FeCl}_2 \cdot 3\text{C}_6\text{H}_4 \cdot \text{CH}_3\text{NH}_2\text{Cl} \cdot 6\text{H}_2\text{O}$	Found.
Chlorine	26.62	26.36 26.68
Iron	8.42	8.00 8.37

Hexaorthotoluidine Chlorferrite, $\text{FeCl}_2 \cdot 6\text{C}_6\text{H}_4 \cdot \text{CH}_3\text{NH}_2\text{Cl} + x\text{H}_2\text{O}$.

From solutions of ferrous chloride and *o*-toluidine hydrochloride in the ratios of 2 : 1–1 : 4, ferrous chloride, toluidine hydrochloride, and double salt may separate, according to the conditions of the experiment. In many cases a mixture of any two, or of all three of the substances, may be obtained. The analyses of the double salt—when the purity of the salt could be relied upon—in all cases, except the one already given, pointed to the compound of the formula



In the first part of this work the solutions containing ferrous chloride and toluidine hydrochloride were boiled and cooled in beakers exposed to the air; so that, where there were second or third crops obtained from the mother-liquors, these were found to be the *hexaorthotoluidine chlorferrate*, already described.

Later, as the difficulties and the importance of the work were realized, the salt was made in an atmosphere of hydrogen, and the mother-liquors were tested for ferric iron; but this subject will be taken up later.

Two solutions of ferrous chloride and *o*-toluidine hydrochloride were made up in the ratios of 2 : 1 and of 3 : 1. These solutions contained respectively 8 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride, and 12 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride; the volume was about 60 cc.

Solution 2 : 1 gave a crop of a double salt before the solution was quite cold. This was filtered off and prepared for analysis. In the morning there was in the mother-liquor a mixture of crystals of ferrous chloride and of a double salt.

Solution 3 : 1 gave a crop of the double salt that seemed to be free from impurities. It was analyzed.

A second solution in the ratio of 3 : 1 was made like that above; from this solution a salt was obtained. The analyses of these salts gave the following results :

	Sol. 2 : 1.	Found for salt from Sol. 3 : 1, No. I.	Sol. 3 : 1, No. II.
Chlorine	27.91	28.78	28.16
	27.92	28.77	28.14
		28.44	28.18
Iron		5.48	5.36
	5.37	5.42	5.39
Ratio of iron to chlorine	1 : 8.23	1 : 8.44	1 : 8.4

These salts gave ferrous hydroxide on adding the salts to solutions of potassium hydroxide.

Both of the mother-liquors of the solutions in the ratio 3 : 1 gave crops of an orange salt, which, on analysis, gave the following results :

	Calculated for $\text{FeCl}_3 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_3 \end{smallmatrix} \text{Cl}_3 \cdot 3\text{H}_2\text{O}$	Found for salt from sol.	
		3 : 1, No. I.	3 : 1, No. II.
Chlorine	29.59	29.25	29.36
Iron	5.20	5.95	5.36

These salts were no doubt the *hexaorthotoluidine chlorferrate*. In the later work—after the salts with *ferric chloride* and *o*-toluidine hydrochloride had been investigated—it was found that the solution of ferrous chloride and *o*-toluidine hydrochloride, on exposure to the air, gave the *ferric* double salt, as in the case of aniline hydrochloride.

Solution in the ratio of 1 : 2.—A solution was made which contained 6.28 grams of crystallized ferrous chloride and 9 grams of *o*-toluidine hydrochloride. This solution separated a crop of silky yellow needles. The dried salt gives a precipitate of ferrous hydroxide, which immediately passes over to the ferric hydroxide, on decomposing it with potassium hydroxide. When heated, the salt gave off toluidine hydrochloride, but no water was detected.

Solution in the ratio of 3 : 1.—A solution was made which contained 18.8 grams of crystallized ferrous chloride and 4.5 grams of *o*-toluidine hydrochloride in about 60 cc. of acid—mostly concentrated hydrochloric acid. The solution gave a crop of crystals which have the light-yellow color when seen from the side and the reddish tint when seen from the ends. 3.4 grams of the salt were obtained. The salt was analyzed.

On further cooling, crystals of ferrous chloride and of a double salt separated. To the solution containing the crystals a quantity of *o*-toluidine was added and the solution was heated. From it there was obtained a crop of the double salt. The dried salt gives off some water and toluidine hydrochloride on heating.

The three salts gave ferrous hydroxide on decomposing them with potassium hydroxide solution. The analyses of the three salts gave the following results :

	Found for salt from sol.		
	1 : 2.	3 : 1.	?
Chlorine	28.28 28.34	26.73 26.87	28.28 28.13
Iron	4.77(?) 5.00	5.74 5.86	5.12 5.15
Water	none found.		slight amount.
Ratio of iron to chlorine	1 : 8.9	1 : 7.36	1 : 8.6

The action of nascent hydrogen was tried on the acid solution of the double salt. When iron wire was dissolved in the acid solution, the dark-yellow liquid changed to a lighter color and there separated a white or colorless salt mixed with toluidine hydrochloride. The salt was in well-shaped crystals, some of which had a feathery form. The crystals and the solutions were transferred to a Florence flask fitted with a Bunsen valve. The solution was kept at the boiling-temperature for about twelve hours ; after standing over night, a crop of the yellow double salt, which shows the two colors, separated above a crop of ferrous chloride, which was in large crystals. 2 grams of the double salt were obtained pure. It gave ferrous hydroxide. On analysis the following results were obtained :

	Found.
Chlorine	28.62 28.45
Iron	5.82 5.87
Ratio of iron to chlorine	1 : 7.8

Preparation of the Salt in an Atmosphere of Hydrogen.

In order entirely to remove any possibility of the formation of ferric chloride in these solutions, the salts were prepared after this time only in an atmosphere of hydrogen. For this purpose a wide-mouth flask was provided with a rubber stopper having 3 holes. Through one of these passed the tube of a reflux condenser, which was provided on the upper end with a Bunsen-valve ; through the other holes passed 2 small bent tubes. One of these tubes was closed by means of a short rubber tube and pinch-cock ; the other was connected with a

hydrogen generator. The object of the closed tube was to permit the concentration of the solution. During the preparation of the salts all the air was driven out of the flask by a current of hydrogen, which was continued until the salt was taken from the flask.

Solution in the ratio of 2 : 1.—A solution was made which contained 4.5 grams of *o*-toluidine hydrochloride and 8 grams of ferrous chloride, part of which was made by dissolving iron wire in the acid solution. The solution was made up to about 100 cc. with hydrochloric acid—strength not noted. The solution was boiled some time and then cooled, but no salt separated. It was then concentrated and cooled at different concentrations without the formation of a salt, until it was reduced to a volume of 25–30 cc. Then, although no salt formed at the ordinary temperature, on cooling in ice-water, 3 or 4 crystals formed; the cooling-bath was now removed but the solution yielded other crystals, about these as nuclei, which finally filled the solution. The formation of these crystals from the cold solution was very interesting. The crystals were a light-yellow color, but showed the two colors. In the dry state the salt had a light-yellow color. 3.8 grams of the salt were obtained, and the analyses gave the following results :

Chlorine	25.99
	25.75
Iron	4.71
	4.55

A second solution in ratio 2 : 1 was made like the last except that the volume was 50–60 cc. On standing over night a yellow salt formed, mixed with fine grains of ferrous chloride, which could not be separated. After heating the solution to dissolve all the salt, and again cooling, only toluidine hydrochloride separated.

A third solution in the ratio of 2 : 1 was made like the other two solutions containing 4.5 grams of toluidine hydrochloride, but the volume was only 40 cc. The solution was boiled about an hour and then left two days with a current of

hydrogen passing through the apparatus. No salt separated, even on cooling with ice-water. The solution was then concentrated somewhat and again cooled with ice-water, when the yellow needles separated in hemispherical masses as in the first "2 : 1" solution. The analysis of this salt gave the following results :

Chlorine	26.13
Iron	5.75

An examination of the analysis of this compound shows that the results—when the percentages of the chlorine are considered—fall into 2 groups ; the first group contains those analyses in which the percentage of chlorine is about 28 ; the second group contains those analyses in which the percentage of the chlorine is about 26. This can be best brought out by presenting the results in tabular form.

With these are given the calculated percentages for the hexaorthotoluidine chlorferrite with and without water of crystallization. It will be seen that the analyses of the salts in the first group, from all the solutions except the solution 1 : 2, correspond very well for the anhydrous salt or for the salt with 1 molecule of water.

		Found for salt from solution in ratio of					
		2 : 1.	3 : 1, No. I.	3 : 1, No. II.	1 : 2.	?	?
Chlorine	27.91	28.78	28.16	28.28	28.28	28.62	
	27.92	28.77	28.14	28.34	28.13	28.45	
Iron	5.37	5.48	5.36	5.00	5.12	5.82	
		5.42	5.39	4.77(?)	5.12	5.77	
Calculated for							
FeCl ₃ .6C ₆ H ₄ < ^{CH₃} _{NH₂} Cl. xH ₂ O.		Anhydrous.		+H ₂ O.		+2H ₂ O.	
Chlorine		28.68		28.17		27.67	
Iron		5.66		5.57		5.44	

The second group corresponds to the same salt with 4 or 5 molecules of water of crystallization. In this group are given the results from the analyses of 2 salts obtained in some later work, still to be described.

		Found. Salts from solutions in the ratios of			
	3 : 1.	2 : 1, No. I.	2 : 1, No. II.	1 : 2, No. I.	1 : 2, No. II.
Chlorine	26.73	25.99	26.13	26.86	26.81
	26.87	25.75		27.00	26.40
Iron	5.74	4.71	5.75	5.27	4.71
	5.86	4.55		5.32	4.83
Calculated for $\text{FeCl}_2 \cdot 6\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2\text{Cl} \cdot x\text{H}_2\text{O}$					
		4 molecules water.		5 molecules water.	
Chlorine		26.73		26.29	
Iron		5.29		5.20	

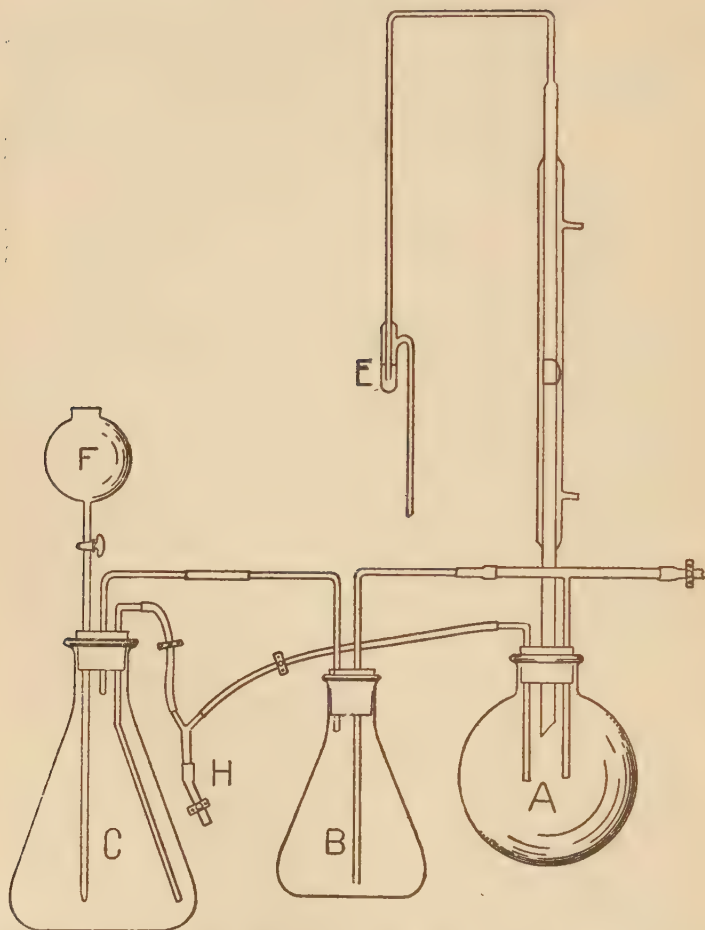
About a year later, after the work on the double salts of ferric chloride and the toluidine hydrochloride was nearly finished—this work was taken up again to see if the results first obtained could be verified. In view of the results which had been obtained by saturating solutions containing the 2 chlorides with hydrochloric acid gas, it was determined to try that method in this case.

This work was carried out in a specially constructed apparatus. The apparatus was so arranged that a solution in the boiling-flask could be kept in an atmosphere of hydrogen, while any one or all of such operations as, boiling with a return condenser, evaporating the solution, boiling off hydrochloric acid gas, or saturating the solution with hydrochloric acid gas, could be performed.

A is a round flask used to hold the solution of the double salt; *B* is an empty flask used as a trap to catch the solution in *A* in case of back pressure; *C* is a hydrochloric acid gas generator, the gas being produced by the action of concentrated sulphuric and on concentrated hydrochloric acid; *D* is the return condenser, and *E* is a mercury trap used to prevent the access of air.

The Y tube at *H* connects the apparatus with a hydrogen generator, so that, by means of the connection shown, all the air could be driven out of the whole system, and a current of hydrogen under slight pressure could be passed through the system.

Solution in the ratio of 1 : 1.—A solution was prepared in the flask *A* by adding to 25 cc. of dilute hydrochloric acid 4.5



grams of *o*-toluidine hydrochloride and 6.28 grams of pure crystallized ferrous chloride. The ferrous chloride nearly all went into solution, while the toluidine hydrochloride remained suspended in the liquid. All of the air was driven out of the apparatus previously to the addition of the ferrous chloride, and the action of the air was thus prevented.

When hydrochloric acid gas was passed into the solution it became warm and all the salts were dissolved. As the solu-

tion became nearly saturated with the gas, a white substance separated, filling the liquid. This seemed to be a mixture; on exposure to the air it rapidly became oxidized. The mother-liquor gave two crops of short, thick, white needles, which, when dried, gave reactions for ferrous iron and for toluidine.

A solution in the ratio of 1 : 4 gave only toluidine hydrochloride, when it was treated as above.

A second solution, in the ratio of 1 : 1 was made by dissolving 1.57 grams of crystallized ferrous chloride and 1 gram of *o*-toluidine hydrochloride in 25 cc. of hydrochloric acid (sp. gr. about 1.12). This was boiled all day with a return condenser, and then cooled in ice-water, but no salt crystallized out. It was then concentrated to about 10 cc., when crystals separated in the form of little balls—probably composed of very fine needles. These gave a reaction for ferrous iron, but no reaction for toluidine was obtained.

A second solution, just like that above, was saturated with hydrochloric acid gas when only toluidine hydrochloride separated.

Solution in the ratio of 1 : 2.—4.5 grams of *o*-toluidine hydrochloride were dissolved in 25 cc. of dilute hydrochloric acid, which formed a saturated solution when cooled. All of the air was driven out of the apparatus by a current of hydrogen, and then 3.65 grams of crystallized ferrous chloride was added to the solution. The solution was warmed to dissolve the salts and hydrochloric acid gas was passed into it. A crop of the crystals separated that looked like toluidine hydrochloride. The solution was again heated and saturated with hydrochloric acid gas, as it cooled in ice-water, but only a small amount of toluidine hydrochloride separated in small compact crystals. The solution was left over night, and in the morning it was quite filled with fine crystals of the double salt, which showed the two colors as before described. The surface layer was taken off and dried; it was then tested for *ferric* iron, but all the tests showed only *ferrous* iron.

The mass of the salt was filtered off and prepared for analy-

sis. The dried salt had a lemon color, and gave tests for iron only in the ferrous state. When heated in the air-bath at 95° , water was given off. The results of the analysis are given with those of the next sample.

A solution in the ratio of 1 : 3 gave only toluidine hydrochloride.

Solution in the ratio of 1 : 2.—A solution was made by dissolving 4.5 grams of *o*-toluidine hydrochloride in 25 cc. of dilute hydrochloric acid and then adding 0.884 gram of pure iron wire. All air was driven out of the apparatus by a current of hydrogen and hydrochloric acid gas was passed into the hot solution, as required, to dissolve the iron wire. While the solution was being cooled to 0° , hydrochloric acid gas was passed into it. It was then left over night, when it came to the temperature of the room. There was then found a crop of fine colorless needles formed in bunches.

The solution was again cooled in ice-water and hydrochloric acid gas passed in to see if there would be any change, but none was observed. It was now boiled two hours with the return condenser, and again saturated with the gas as it cooled. After standing over night a large amount of a pure salt had separated in fine crystals, nearly filling the solution. When the flask was opened, the upper layer became slightly yellow, and before the salt could be dried it had the same yellow color as the previous sample. The mother-liquor fumed with hydrochloric acid. The salt, on heating at 100° , gave off water very quickly and in quite large amount. The analyses of these two salts gave the following results :

	Calculated for $\text{FeCl}_2 \cdot 6\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \cdot 4\text{H}_2\text{O}$	Found.	
		No. I.	No. II.
Chlorine	26.73	26.86 27.00	26.81 26.40
Iron	5.29	5.29 5.32	4.71 4.83

Further work on Aniline Hydrochloride and Ferrous Chloride.
—After the composition of the hexaorthotoluidine chlorferrite was established, it was thought that by working with solutions of ferrous chloride and aniline hydrochloride containing

a smaller proportion of ferrous chloride, a salt might be obtained which would contain a larger proportion of aniline hydrochloride, *i. e.*, the analogue of the hexaorthotoluidine chlorferrite. The work was carried out as described under the orthotoluidine compound.

From a solution containing one molecule of ferrous chloride to six molecules of aniline hydrochloride, there was obtained a double salt in the form of fine needles. When these crystals were on the filter, they changed their crystalline form from fine needles to plates. These were prepared for analysis. They were freed from the last trace of hydrochloric acid by standing over solid potassium hydroxide in a desiccator filled with hydrogen. A sample of the salt was heated at 98° , when a rather small amount of water was given off.

The analysis gave the following results :

	Found.
Chlorine,	31.13
	30.98
Iron,	6.75
	6.76
Ratio of iron to chlorine	1 : 7.26

From a second solution in the ratio of 1 : 6, a crop of the fine needles separated ; but they could not be obtained in condition for analysis.

A third solution, in the ratio of 1 : 6, gave a mixture of the fine needles and of the plates. A solution in the ratio of 1 : 4 gave a crop of crystals that was composed of two layers ; in the upper layer were the fine needles, while in the lower layer were the plates. These were separated rather roughly and analyzed.

The sample composed mostly of the fine needles gave results pointing to the dianiline chlorferrite. The layer composed mostly of the plates gave results for a mixture of the lower salt and of a higher salt.

Other attempts were made to get a higher salt, but the crystals could not be obtained in pure condition.

However, the indications are that a higher salt of aniline hydrochloride and ferrous chloride may be formed under proper conditions.

Conclusion.

From this study it was found that the chlorides of iron do not form the normal double chlorides with the aromatic substituted ammonias. While from ferric halides and ammonium halides the two salts formed are: $\text{FeCl}_3 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ and $\text{FeBr}_3 \cdot \text{NH}_4\text{Br} \cdot 2\text{H}_2\text{O}$; only aniline and *m*-toluidine gave the 1:2 salt, while no salt of the 1:1 type was obtained. The 1:3 salt was obtained from meta and from para-toluidine hydrochloride.

There seems to be a greater similarity between *o*-toluidine and aniline, both giving the 1:6 salts hexaniline and hexa-orthotoluidine chlorferrate, than between *o*-toluidine and the other toluidines.

With ferrous chloride and *o*-toluidine hydrochloride there is produced a double halide of an entirely new type.



The salts which fall under the extension of the law for double halides are,



BIOGRAPHICAL.

The author of this dissertation was born in Jersey City, N. J., April 12, 1867. He was prepared for college at a private school in Rahway, N. J., and at Hasbrouck Institute, in Jersey City. In 1886 he entered the University of the City of New York, receiving the degree of B.S. in 1890. During the years 1890-92 he pursued graduate study in chemistry and in physics at his Alma Mater. In 1892 he received the degree of M.S. He held the Scientific Fellowship and acted as Demonstrator in the Chemical Laboratory during 1891-92. In the Fall of 1892 he came to the Johns Hopkins University, where he has since continued his work in chemistry with physics and mathematics as subordinate subjects.

